

# Flory-Huggins Model of Equilibrium Polymerization and Phase Separation in the Stockmayer Fluid

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The competition between chain formation and phase separation in the Stockmayer fluid (SF) of dipolar particles is analyzed using a renormalized Flory-Huggins model of equilibrium polymerization. Calculated critical properties ( $T_c$ ,  $\phi_c$ ,  $Z_c$ ) for the SF compare favorably with simulations over a wide range of the dimensionless dipolar (or “sticking”) energy  $\mu^*$ . We find that the polymerization transition preempts phase separation for a large  $\mu^*$ , i.e.,  $(\mu^*)^2 > 22$ .

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The novel properties of many “complex” fluids stem from a competition between the influences of van der Waals (vdW) interactions and *directional* interactions that may arise from dipolar, multipolar, and induced dipole forces and/or the discrete atomic structure of complex molecules [1,2]. When attractive vdW interactions predominate, there is a tendency towards simple phase separation. When these two types of interactions have comparable strengths, their interplay often leads to the self-organization of particle clusters that exist in a state of *dynamic equilibrium*, as observed in many polyelectrolyte, charged colloid, protein, surfactant, and nanoparticle dispersions [3].

No general predictive theory exists for the coupling of dynamic clustering transitions and phase separation processes that occur in these fluids [4]. However, important insights emerge from recent simulations of charged [5–7] and dipolar particle fluids [8,9], such as the Stockmayer fluid (SF) [8–10] [a fluid of particles with a Lennard-Jones (LJ) potential and a superimposed dipolar interaction]. In particular, simulations of the SF indicate the development of transient linear chains of dipoles for sufficiently large dipole strengths. Simulations for mixtures of positively and negatively charged spheres exhibit the formation of dipolar or multipolar structures that then form either linear or branched “polymers,” depending on the charge and size asymmetry of the ions [5,7]. Branched equilibrium polymers have also been found in simulations of platelet particles with quadrupolar interactions introduced to model gelation in exfoliated clay solutions [11]. Particular interest in the SF has been stimulated by claims [9,10,12] that the critical temperature  $T_c$  ceases to exist in this system if the dipolar interaction is sufficiently large relative to the vdW interaction, and a number of arguments attempt to rationalize this theoretically unexpected phenomenon [13,14].

The competition between chain formation and phase separation in the SF is analyzed here using a Flory-

Huggins (FH) lattice gas model. Our primary goal lies in relating the parameters of the SF intermolecular potentials to the parameters of a minimal FH model. The FH approach can be generalized to describe the molecular structure of the associating species (when a lattice model is adequate), branching of polymer clusters [15], and constraints on the polymerization process (activation, chemical initiation) [16], providing a versatile tool for modeling a large variety of associating systems. The present treatment approximates a system with long-range interactions by a FH model with only short-range, directional interactions that induce the clustering processes to a degree governed by the strength of the long-range interactions [14,17,18]. We avoid relying on asymptotic results for infinite dipolar energies to estimate the model parameters. Instead, we renormalize the FH vdW interactions to account for the dipolar contributions using exact analytical results for the second virial coefficient of the SF [18]. Thus, our treatment of dipolar fluids differs from that of Tavares *et al.* whose living polymerization theory applies only to the limit of infinite dipolar energy.

The simplest model of equilibrium polymerization postulates that each molecule or particle can *freely associate* to form linear polymer chains under conditions of thermodynamic equilibrium. Analysis of this model [16] shows that the thermodynamic properties of the system are unaffected by details of chain scission and fusion processes. Chain stiffness serves to change the entropy of polymerization [3,16], but does not produce qualitative effects on the thermodynamics at lower concentrations where liquid crystal type ordering is absent [19].

The FH model system is composed of a monomer species  $M$  whose association is governed by a free energy of polymerization  $\Delta f_p = \Delta h_p - T\Delta s_p$  or, equivalently, the enthalpy  $\Delta h_p$  and entropy  $\Delta s_p$  of polymerization. The polymers form and disintegrate in *dynamic equilibrium*. The polymerization process is characterized by the *equilibrium reaction*,

$$M_j + M_k \leftrightarrow M_{j+k}, \quad j, k = 1, 2, \dots, \infty, \quad (1)$$

where  $K_p = \exp(-\Delta f_p/k_B T)$  is the unique equilibrium constant for all  $j$  and  $k$ . The usual isotropic vdW interactions are represented by the parameter  $\chi = \varepsilon_{\text{FH}}/T$  of the FH model [9]. The concentration of the associating species in the FH treatment is the product of the particle number density and the lattice cell volume, defined by the hard-core exclusion volume just as in the vdW gas model [20]. All properties analyzed below are expressed as dimensionless ratios, so that the lattice cell volume and other “nonuniversal” parameters do not enter explicitly.

The Helmholtz free energy  $F$  per lattice site (volume) for the free association lattice gas is given by [16]

$$F/k_B T = (1 - \phi) \ln(1 - \phi) + \phi \ln \phi_f + \chi(1 - \phi)\phi + f_A, \quad (2)$$

where  $\phi$  and  $\phi_f$  are the monomer volume fractions before and after polymerization, respectively. The association contribution  $f_A = (z\phi_f A/2)/(1 - A)^2$  is a function of  $\phi_f$  and the association parameter  $A \equiv \phi_f K_p$ . The lattice coordination number is chosen as  $z = 6$ , corresponding to a cubic lattice. The equilibrium monomer concentration  $\phi_f$  is determined numerically from the mass conservation equation  $\phi = \phi_f + f_A(2 - A)$  [16].

The SF is an idealized model of a dipolar gas or dipolar particle dispersion in a continuum fluid. (See [21] for a review.) The point particles (with dipole moments  $\mu$ ) interact with a Lennard-Jones potential (specified by well depth  $\varepsilon_{\text{LJ}}$  and interaction range  $\sigma$ ). The reduced dipole energy is simply  $\mu^* = (\mu^2/\varepsilon_{\text{LJ}}\sigma^3)^{1/2}$  ( $k_B \equiv 1$ ). In conformity with other attempts to describe the polymerization in the SF, we assume that the long-range interactions between individual dipoles are compensated in the particle clustering process and, thus, are effectively subsumed into the interaction parameters ( $\Delta h_p, \Delta s_p, \varepsilon_{\text{FH}}$ ) of the FH model of equilibrium polymerization. Arguments have been given supporting this approximation [18], which is normally used to model equilibrium polymerization in experimental systems.

Chains are the preferred form of clusters in the SF because the mutual potential energy of interaction is minimized when spherical dipolar particles of radius  $\sigma$  align head to tail. The energy minimum at this configuration equals  $2(\mu^2/\sigma^3)$  and provides the first natural approximation to the “sticking energy”  $\Delta h_p$  of the FH model through  $\Delta h_p/R \approx 2(\mu^2/\sigma^3)$  [10,18], where the gas constant  $R$  enforces dimensional consistency. Moreover, the correspondence  $\Delta h_p/R \approx 2(\mu^2/\sigma^3)$  implies that the calculated second virial coefficient  $A_2$  for the FH model [16] is consistent with the exact asymptotic scaling of  $A_2$  for the SF in large dipolar energy limit [22].

Figure 1 summarizes Monte Carlo (MC) results for  $T_c^{\text{SF}}(\mu^*)$  of the SF that are normalized by the critical temperature for the LJ fluid,  $T_c^{\text{LJ}} = T_c^{\text{SF}}(\mu^* = 0) \equiv T_{c,0}^{\text{SF}}$ .

Triangles denote the data of van Leeuwen and co-workers [8,9], and circles designate the data of Stevens and Grest [10]. The MC data [10] for  $T_c^{\text{SF}}(\mu^*)/T_{c,0}^{\text{SF}}$  exhibit a “knee” at  $(\mu^*)^2 \approx 2$  (see [8–10]) and a linear variation with  $(\mu^*)^2$  for  $(\mu^*)^2 \geq 2$ . The knee is also characteristic of the dependence of  $T_c$  on  $(|\Delta h_p|/R)/2\varepsilon_{\text{FH}}^0$  in the free association model, and the position of the knee depends on  $\Delta s_p$  [16].

Before comparing predictions of the FH model with simulations for the SF, the parameters of both models must be interrelated. The vdW interaction strength for the LJ fluid (i.e., for the SF with vanishing  $\mu^*$ ) is  $\varepsilon_{\text{LJ}}$ , and its counterpart in the FH model is  $\varepsilon_{\text{FH}}^0$ . A relation between  $\varepsilon_{\text{LJ}}$  and  $\varepsilon_{\text{FH}}^0$  is determined by equating the theta temperatures  $T_{\theta,0}^{\text{SF}} = T_{\theta,0}^{\text{FH}}$  at which  $A_2$  vanishes [23]. This condition is suitable because  $T_\theta$  far exceeds  $T_c$  and can be calculated exactly for the SF [24,25] and very precisely for the LJ fluid as  $T_\theta^{\text{LJ}} \equiv T_{\theta,0}^{\text{SF}} = 3.417\,928\,02(3)\varepsilon_{\text{LJ}}$  [26]. Since  $T_\theta$  for a monomer lattice fluid equals  $T_{\theta,0}^{\text{FH}} = 2\varepsilon_{\text{FH}}^0$ , we obtain  $\varepsilon_{\text{FH}}^0 \approx 1.709\varepsilon_{\text{LJ}}$ .

Combining the correspondence between  $\varepsilon_{\text{LJ}}$  and  $\varepsilon_{\text{FH}}^0$ , the definition  $\mu^* = (\mu^2/\varepsilon_{\text{LJ}}\sigma^3)^{1/2}$ , and the relation  $\Delta h_p/R \approx 2(\mu^2/\sigma^3)$  yields scaling between the main parameters of the FH and SF models,

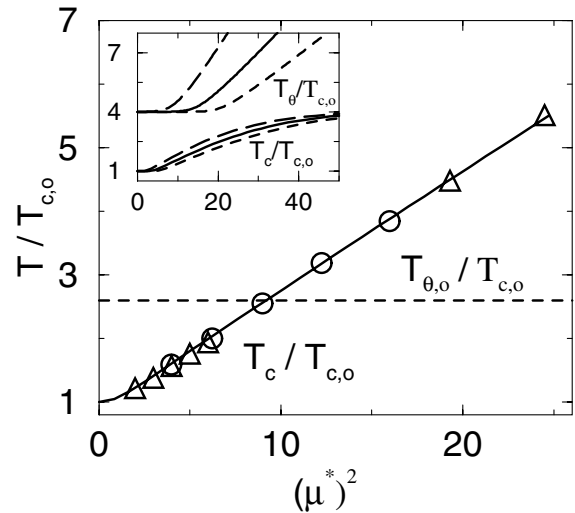


FIG. 1. Comparison of reduced critical temperature  $T_c/T_{c,0}$  and reduced theta temperature  $T_\theta/T_{c,0}$  of the SF between MC simulations and renormalized FH model predictions. Triangles denote MC data of van Leeuwen *et al.* [8,9], and circles designate data of Stevens and Grest [10].  $T_{c,0}$  and  $T_{\theta,0}$  refer to data for the LJ model. The uncertainty in MC simulations for  $T_c/T_{c,0}$  is about  $\pm 0.01$  [10]. The strong dependence of  $T_c$  on  $\mu^*$  in the MC simulations cannot be reproduced within the FH model without renormalizing the vdW interactions. As emphasized in the inset, when the vdW interactions are *not renormalized*, i.e.,  $\varepsilon_{\text{FH}} = \varepsilon_{\text{FH}}^0$ , the predicted  $T_c/T_{c,0}$  cannot exceed  $T_{\theta,0}/T_{c,0}$ . Long-dashed, solid, and short-dashed curves correspond to  $\Delta s_p = -75, -105$ , and  $-135$  J/(mol deg), respectively.

$$(\mu^*)^2 \approx 1.709[|\Delta h_p|/R]/2\varepsilon_{\text{FH}}^0, \quad (3)$$

enabling the comparison of these two models. Inspection of Fig. 1 reveals that  $T_c^{\text{SF}}(\mu^*)$  can significantly exceed  $T_\theta^{\text{LJ}}$  (dashed line). For instance,  $T_\theta^{\text{LJ}}/T_c^{\text{LJ}} \approx 2.6$ , whereas  $T_c^{\text{SF}}/T_c^{\text{LJ}} \approx 5.5$  for  $(\mu^*)^2 = 24.6$  [23]. Describing the elevation of  $T_c^{\text{SF}}$  above  $T_\theta^{\text{LJ}}$  within the FH lattice model requires a renormalization of the effective FH vdW interaction  $\varepsilon_{\text{FH}}^0$  to incorporate contributions from dipolar interactions [17]. This need is also evident from the inset of Fig. 1, which demonstrates that the critical temperature  $T_c^{\text{FH}}$  for the unrenormalized FH model (i.e., with  $\varepsilon_{\text{FH}}^0$  instead of  $\varepsilon_{\text{FH}}$ ) never surpasses  $T_\theta^{\text{FH}}$  for this case.

Exact calculations for  $A_2$  of the SF [24,25] provide a recipe for renormalizing  $\varepsilon_{\text{FH}}$ . First, tabulations of  $A_2$  for the SF in Appendix II-A of Ref. [27] as a function of  $\mu^*$  and  $T$  enable determining  $T_\theta^{\text{SF}}(\mu^*)$ . The shift of the theta temperature  $\Delta T_\theta^{\text{SF}} \equiv T_\theta^{\text{SF}}(\mu^*) - T_\theta^{\text{SF}}(\mu^* = 0)$  due to the dipolar energy is approximately a linear function of  $(\mu^*)^2$  in the regime where the data are tabulated [i.e.,  $(\mu^*)^2 \leq 2$ ]. Specifically, we find

$$\Delta T_\theta^{\text{SF}}/T_c^{\text{SF}}(\mu^* = 0) \approx 0.27[(\mu^*)^2 - (\mu^*)_0^2],$$

where  $(\mu^*)_0^2 = 0.48$ . On the other hand, the inset of Fig. 1 shows that  $T_\theta^{\text{FH}} = 2\varepsilon_{\text{FH}}^0$  is constant for the bare FH model (with  $\varepsilon_{\text{FH}} = \varepsilon_{\text{FH}}^0$ ) in the *weak coupling regime*. Hence, the renormalization of  $\varepsilon_{\text{FH}}^0$  is established by equating  $\Delta T_\theta^{\text{SF}}/T_c^{\text{SF}}$  and  $\Delta T_\theta^{\text{FH}}/T_c^{\text{FH}}$  for  $(\mu^*)^2 - (\mu^*)_0^2 > 0$ . Defining a multiplicative renormalization  $\varepsilon_{\text{FH}}(\mu^*) = \varepsilon_{\text{FH}}^0[1 + \delta(\mu^*)]$  leads to the relation

$$\delta(\mu^*) = \Delta T_\theta^{\text{FH}}/T_{\theta,0}^{\text{FH}}. \quad (4)$$

Since  $\Delta T_{c,0}^{\text{FH}}/T_{\theta,0}^{\text{FH}} = 1/4$ , Eq. (4) becomes

$$\delta(\mu^*) = 0.065[(\mu^*)^2 - (\mu^*)_0^2]. \quad (5)$$

This  $\delta(\mu^*)$  exhibits a weak power law  $\delta(\mu^*) = 0.04(\mu^*)^4$  dependence on the dipolar energy for  $(\mu^*)^2 \leq 0.1$ , but we neglect this miniscule renormalization of  $\varepsilon_{\text{FH}}^0$  for small  $\mu^*$  [i.e., choose  $\delta(\mu^*) \equiv 0$  for  $(\mu^*)^2 \leq (\mu^*)_0^2$ ].

All the lattice model parameters are now fixed except  $\Delta s_p$ . A rough estimate of  $\Delta s_p$  can be obtained by using our finding [16] that the knee in  $T_c^{\text{FH}}(\Delta h_p)$  in the inset of Fig. 1 occurs for  $\Delta h_p$  on the order of  $\Delta s_p/4R$ . Converting this turnover value to  $(\mu^*)^2$  and equating it with that in the SF data [ $(\mu^*)^2 \approx 2$  to 3] yields  $\Delta s_p/R \approx 5$ , which agrees in order of magnitude with Rowlinson's [25] estimate of  $\Delta s_p$  for a number of dipolar gases (acetonitrile, methyl chloride, acetaldehyde, water, ammonia). In the following comparisons of the FH and SF models,  $\Delta s_p$  is treated as an adjustable parameter that must be consistent with these approximate estimates.

Figures 1 and 2 compare the SF simulations and FH model predictions for the SF critical temperature  $T_c(\mu^*)$  and critical composition  $\phi_c(\mu^*)$ . Both quantities are normalized by their respective values for the LJ fluid to

minimize model dependent and nonuniversal effects. The fits to the SF  $T_c$  are made for the idealized stiff and fully flexible chain models using  $\Delta s_p = -49$  and  $-71$  J/(mol deg), respectively, while no adjustable parameters enter into the computation of  $\phi_c(\mu^*)$  in Fig. 2 [8,9]. The agreement between the simulations and the FH model predictions is quite respectable for  $\phi_c(\mu^*)$ , given the considerable uncertainty in determining  $\phi_c(\mu^*)$  from the very flat MC coexistence curves. The reduced *critical compressibility factor*,  $Z_c \equiv \Pi_c/T_c\phi_c$ , where  $\Pi_c$  is the pressure at the critical point, is another basic critical property that is analyzed in the inset of Fig. 2. The FH model predicts the correct trend in the variation of  $Z_c/Z_{c,0}$  with  $(\mu^*)^2$  [where  $Z_{c,0} = Z_c(\mu^* = 0)$ ], but the uncertainties in the MC estimates of this property are even larger than those for  $\phi_c(\mu^*)$ , as indicated in [8,9]. The MC data are insufficient to decide whether the stiff or flexible chain models are most accurate, but the differences between the models are not large.

The competition between phase separation and polymeric association in the SF is further illustrated in Fig. 3 which depicts the spinodal curves and polymerization lines for  $(\mu^*)^2 = 1, 10$ , and 22. These values of  $(\mu^*)^2$  lie below and above the “crossover value”  $(\mu^*)^2 \approx 2$  and near the estimated critical dipolar interaction  $(\mu^*)^2 \approx 25$  where  $T_c$  has been claimed to “disappear” [10]. The polymerization temperature  $T_p(\phi)$ , which is defined by a specific heat maximum [3,16], lies well below  $T_c$  when  $\mu^*$  is small, but coincides with  $T_c$  for  $(\mu^*)^2 \approx 22$ . The SF spinodal curves flatten and become

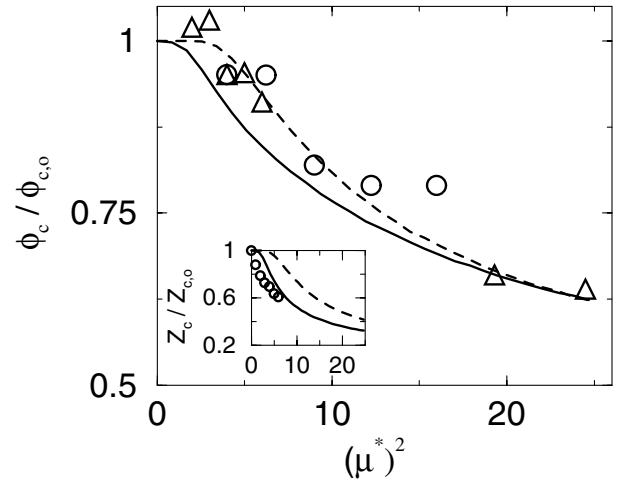


FIG. 2. Comparison of reduced critical composition  $\phi_c/\phi_{c,0}$  of the SF between MC simulations and renormalized FH model predictions. Triangles and circles refer to the same data as in Fig. 1. The uncertainty in MC simulations for  $\phi_c/\phi_{c,0}$  is about  $\pm 0.033$ , roughly twice the size of the triangles ( $\approx 0.03$ ) [8]. Solid and dashed lines are FH model predictions for stiff and fully flexible chains, respectively. The inset provides a corresponding comparison for the reduced critical compressibility  $Z_c/Z_{c,0}$ . Circles are data of van Leeuwen [8].

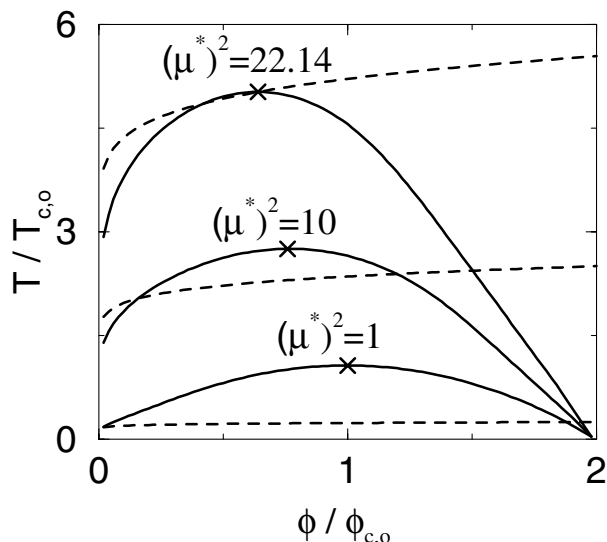


FIG. 3. Spinodal curves and polymerization lines of the SF for different values of the dimensionless dipolar energy  $(\mu^*)^2 = 1, 10$ , and  $22$ . Both  $T$  and  $\phi$  are normalized as in Figs. 1 and 2.

more asymmetric with increasing  $\mu^*$ . This increased anisotropy of the phase boundary stems from the polymeric nature of the fluid in the critical region.

A major unresolved aspect of the MC simulations of the SF concerns claims of a disappearing critical point for  $(\mu^*)^2$  greater than a “critical” value near 25 [10]. Our calculations for  $(\mu^*)^2 = 25$  demonstrate that the polymerization transition for the critical composition occurs at a higher temperature than  $T_c$ . This result is consistent with the finding of the simulations that long chains are the most conspicuous structures observed in this regime of large  $\mu^*$  [9,10,12]. Since long chains persist on long time scales for  $T < T_p(\phi_c; \mu^*)$ , configurational sampling by conventional MC effectively becomes *impossible*.

Further insight into the critical behavior of the SF should emerge from studies of related associating fluids. For example, recent direct imaging measurements for nanoparticle dispersions of magnetic particles in decalin suggest that the system is a close realization of the SF [28]. The dipole interaction varies with particle size [28], and the effective vdW interaction can be tuned in colloidal suspensions [29]. Preliminary results for the restricted primitive model with vdW interactions indicate that  $T_c$  and  $\phi_c$  exhibit a similar variation to the critical parameters for the SF model when  $(\mu^*)^2$  is replaced by the ratio of Coulombic charge and vdW energies [30].

The SF model is prototypical of equilibrium molecular self-organization. This Letter describes how the interaction parameters governing this phenomenon are related to molecular interactions and how the coupling between polymerization and phase separation leads to the emergence of critical behavior resembling that of high molecular weight polymer solutions with large clustering

interactions. Although our equilibrium theory implies that  $T_c$  formally exists for all  $(\mu^*)^2 > 0$ , equilibration may not be easily attainable in simulations for which  $T_p(\phi_c; \mu^*) > T_c(\mu^*)$ .

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